



DOWNEY

Solubility of set Portland cement

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SOLUBILITY OF SET PORTLAND CEMENT

BY

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A. B. University of Illinois, 1909

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

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IN CHEMISTRY

IN

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Elzy Franklin Downey

ENTITLED Solubility of Set Portland Cement

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science In Chemistry

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Recommendation concurred in:

Committee

on

Final Examination



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INTRODUCTION

When any new material begins to come into use there is a general tendency to look on it at first with distrust and users are unwilling to give it a trial even in places where it seems suitable. While, on the other hand, after it has been tried and found well adapted to certain conditions people are apt to go to the opposite extreme and think that because a given material meets the requirements for some places and under certain conditions, it can be used with equal success under all circumstances. This seems to be the case with Portland cement. During the past fifteen years it has come more and more into general use until at the present time there are advocates for its adoption in almost every conceivable situation.

While Portland cement has been employed very successfully in numerous pieces of construction work and under a variety of conditions, it does not follow that it can be used with equal success in all circumstances. A few examples of the doubtful places for which concrete has been recommended will illustrate this point. It has been proposed to make acid vats of concrete. There is another instance where a man wrote to one of our prominent cement journals, asking if it would be advisable to use concrete, where fire-brick are really essential, to make a boiler setting and the editor promptly replied that it would be all right. Concrete is also used in the manufacture of drain tile, sewer pipe, septic tanks, etc., where it is exposed not only to the action of carbonic acid and some of the organic acids but often to solutions of the stronger acids as well. During recent years concrete has been employed to a great extent in construction work exposed to sea-water but it is claimed by many able investigators that salt-water disintegrates cement.

It has long been known and it is now admitted by most people that set Portland cement is readily dissolved by such acids as hydrochloric and sul-



phuric but it is a disputed question as to whether it is soluble to any appreciable extent in weak acids such as carbonic. Much has been said and written on both sides of this question, but from an examination of the literature on the subject it seems that most of what has been written is based on speculation and theoretical considerations and not on actual quantitative experiment. It was with the hope of throwing more light on this by obtaining additional data that this work was undertaken.





## H I S T O R I C A L

### PART I.- SOLUBILITY IN SALT WATER.

The question of the solubility of Portland cement in salt water is one which has aroused a great deal of discussion during recent years and it has been the subject of much investigation both in Europe and America. Engineers are using concrete quite extensively in constructing piers, abutments, dock walls, etc., along the sea coast, where it comes in contact with the salt water continually. The question, therefore, of its action on the concrete, is a most important one. As might be expected, those who have made a careful investigation of this subject do not agree as to just what effect the salt water does have. There are numerous examples where cement construction along the sea coast has become badly deteriorated in a comparatively short time. Some investigators attribute this wholly to the effect of frost, while others are equally positive that the deterioration is entirely due to chemical action.

A good example of this is to be found in the concrete dock wall at the Charleston navy yard in Boston, views of which are given in Engineering News, Vol. 60, page 238.<sup>16</sup> The portion shown in the views was built in 1901 under the direction of the Bureau of Yards and Docks of the U. S. Navy Department-, a bureau that has the reputation for the most careful and thorough work. The docks are located in the tidal salt water of Boston Harbor, which at this point is not highly polluted with sewage or factory waste, but which is subjected to considerable freezing weather and a 10 foot range of tide. The concrete portion of the docks was constructed with all the care for which the Bureau is noted.

The government authorities on the work have no explanations to make as to the cause of the disintegration, merely giving the facts in the case. It is well to note, however, that the decomposition occurred probably in a porous concrete as it was mixed and laid dry with no especial effort toward density or



waterproofing, and that the structure is in tidal sea-water subjected to alternate freezing and thawing and finally that damage has been done mainly between the high and low water levels.

Mr. M. C. Tuttle, Secretary of the Aberthaw Construction Company, in speaking of this wall is quite positive the disintegration is due to the action of frost, and says that in all cases which he has examined the disintegration of concrete can be as readily explained by frost action as by decomposition of cement, and without asserting that every case can be explained by frost action or by bad concrete, he calls attention to the conditions actually existing in all tidewater concrete.<sup>20</sup> On any work located in tidewater the surfaces between high and low tide are alternately wet and exposed to the air once every twelve hours. In cold climates for many weeks of each year an exposure of an hour or two will freeze several inches into the surface of any masonry. The action of the tide necessarily occurs only in salt water and accordingly such alternate freezing and thawing as often as once in twelve hours seldom occurs in any location where the water is fresh. If water could get into a crack in the hardest of rocks and alternate freezing and thawing should occur once in every twelve hours for a long period it is difficult to imagine anything but splitting or spalling occurring at this point. It is common enough to see the surface of sand stone peeling off in layers under this action. In concrete there is no grain as there is in rock and accordingly the splitting action would follow irregular lines and would amount to a general surface disintegration wherever the frost could act.

On the other hand, Dr. W. Michaelis Jr., in referring to the same wall is equally positive that the deterioration is due to chemical action.<sup>21</sup> He predicts that many similar cases of disintegration of Portland Cement will be witnessed in this country during the next decade, as the destruction of Portland cement through the injurious action of sea-water is merely a question of time. Now, in Europe, says Michaelis, experience shows Portland cement concrete used





in harbor construction may resist the action of sea-water sometimes for a considerable length of time, but the softening of the surface of the concrete and the subsequent disintegration of the mortar are bound to come in time, that is to say, if not after a period of ten years, certainly within the second or third decade. The sulphuric acid salts contained in the sea-water combine with the calcium oxide and with the alumina of the Portland cement and destroy the cohesion of the mortar by a process of crystallization. Within the dense conglomerate of dried-out colloids or "mineral glues" which constitute the hardened cement, crystals are formed. These crystals cause distension of the mortar and allow the sea-water to penetrate into the interior until, in time, the whole block or wall or pier is destroyed. Such disintegration can be observed after a few years with every concrete block submerged in sea-water no matter how good the brand of Portland cement used or how well the concreting was done.

One of the very able investigators as to the cause of the disintegration of cement by sea-water is Le Chatelier.<sup>3</sup> He maintains that chemical actions of salt water have different effects on hardening of cement. They may simply bring about a softening of the mass through the formation of compounds having a gelatinous consistency the cement then losing its hardness and succumbing easily to mechanical agencies; or they may be accompanied by swelling and cracking until the material is wholly destroyed. He also claims that the decomposition of cement is an effect of two successive actions. The removal of lime by diffusion, which destroys the solidity of the material and increases its porosity, and the swelling and disintegration of the weakened mass caused by the attack of calcium sulphate. His experiments appear to establish the fact that all the phenomena of decomposition which occur when cements are exposed to sea-water depend upon the action of a little impervious skin which is in a state of perpetual transformation. The conclusions that he establishes are



the following: 1. All the active elements in cements, lime, aluminates and silicates are decomposed immediately upon coming in contact with the magnesium salts of the sea-water, yielding soluble chlorides and sulphates of calcium, and so bringing all the lime present into a state of solution. 2. When calcium sulphate found in natural waters or formed by interaction of magnesium sulphate and the calcium compounds of cement react with calcium aluminate, it produces a calcium sulph-aluminate whose crystallization gives rise to a swelling and cracking of the material, due to the greater volume as this compound crystallizes with 30 molecules of water of crystallization. 3. Penetration of marine salts takes place in two different ways; sea-waters penetrate en masse through all the flaws in the points of masonry and through the crevices in the stones and bricks themselves. Most of the flaws of workmanship are unavoidable. From the present aspect, the normal porosity of cement plays only a secondary part in the process. Afterwards, when cement is sound, circulation of, and attack by, sea-water occurs almost exclusively by a process of diffusion, being the more rapid as the normal porosity of the cement is greater. 4. All phenomena of decomposition in sea water are at the mercy of a superficial film of extreme tenuity whose impermeability tends to prevent or rather hinder diffusive action but whose expansion caused by calcium sulph-aluminate, promotes swelling of material and cracks through which the salt water soon penetrates in quantity.

In a report made by a committee of the Railway Superintendents of Bridges and Buildings of America, the committee had sent out about forty circulars to as many members of the association, asking their experience in the following subjects:<sup>8</sup> 1. Concrete made in air and deposited direct in sea-water. 2. Concrete deposited direct in sea-water. 3. What effect has the frost on concrete where the tide rises and falls on it? Replies received from the vicinity of New York favored concrete made in air and sunk in sea-water, while those from the vicinity





of Boston favor concrete deposited directly into the sea. All replies, however, seemed to indicate that most concrete between high and low-water marks disintegrate more or less rapidly, especially when there is frost. One member stated that he had secured very good results by making cement blocks on the shore with fresh water and then placing them in position.

J. Bied and Vieviere made tests on the action of calcium sulphate (Sat.Sol.), Magnesium Sulphate, 1.2 per cent and artificial sea-water upon cement mortars especially those containing artificial puzzolans, such as dehydrated alumina. Calcium sulphate was most destructive, no cement tested having withstood its action for five years.<sup>24</sup> Addition of puzzolans increases the resistance to the destructive action, blast furnace slag being less efficient for this purpose than calcined alumina. Cements low in Aluminum are readily attacked by calcium sulphate but not by  $Mg SO_4$  solution. Highly silicious cements are almost indestructible in  $Mg SO_4$  solution. Admixture of dehydrated clay is the only known means of resisting the attack of  $Ca SO_4$ .

W. B. Mackenzie, Chief Engineer, Inter-colonial Railway of Canada, says that concrete has been used in eight different places in clear sea-water along this railway, and disintegration of the outer skin has taken place in every case from one-eighth of an inch to six inches deep.<sup>14</sup> It has been used principally to encase stone piers and abutments in thicknesses of one or two feet. At one bridge the casing has been renewed near low-water and at another it has been three times renewed in six to eight years. The concrete mixture is generally 1 : 2 : 4 using the best Portland cement.

In the inland sea of Baddeck C. B. where tide rises only six inches, a concrete culvert four years old is undercut three feet at two corners for a height of eighteen inches, although the concrete is of first class quality. In the Halifax dry dock, the broken face of the concrete has been chipped off and a



band of artificial brick several feet wide now appears around the dock. He further says, "I feel quite safe in saying that the best concrete between high and low-tide marks in clear sea-water will not retain a respectable face in this climate for any great length of time and in a few years will require to be repaired or renewed."

Mr. T. B. Shertzer carried out a series of experiments (1907) with a view to finding the effect of salt water on concrete.<sup>19</sup>

A set of standard briquettes 1 : 3 were made, mixed with fresh water, half of these were stored in fresh water and half in salt water in the laboratory after being twenty-four hours in moist air. A second set were mixed with salt water and stored in the same way, and a third set were made mixed with fresh water, one third of them being stored in the laboratory in fresh water, a second third buried in the sand of the filling about a foot below the surface, and the rest placed in a crate fastened to a pile at about half-tide elevation so that they would be submerged and exposed to the air alternately and for about equal periods of time. A set of three 12 inch cubes were mixed in the laboratory, one of these was dropped to the bottom in about 10 feet of water, the others left on the ground. Lastly a set of blocks 4 x 4 x 12 inches were made of 1:2:4 and 1:2 1/2:5 concrete. Lots of these were allowed to dry in air for one, six and twelve days and were then put into crates secured to piles at mean tide elevation. All of this work was done in the Spring of 1907.

The briquettes of the first two cases i.e., those mixed with fresh and salt water and stored in the laboratory, were tested in the machine at one, two and six months and little or no difference found in them. In the briquettes of the third class, those stored in the filling and those stored in the laboratory showed little or no difference up to the sixth month, but those briquettes left in the filling for a year test showed swelling and cracking after about ten months.





The briquettes stored at mean tide disintegrated entirely in about three months. The 12 inch cube was removed from the bottom of the river after being submerged for nearly a year and was found in perfect condition, as were also the two cubes left lying on the surface of the ground. The 4 x 4 x 12 inch blocks retained their sharp edges and remained in perfect condition throughout the summer but began to disintegrate with the setting in of cold weather and before the winter was over had crumbled to mere shapeless masses. The conclusions which he drew from his experiments were: 1. Concrete is effected by salt water only in cold weather and then only in such portions as lie between tidal ranges and come in contact with water. 2. That the decomposition is due to freezing and thawing. 3. It is perfectly safe to use concrete in salt water when it will be entirely and perpetually submerged.



## PART II.\_ SOLUBILITY IN DRAINAGE SOLUTIONS.

The use of concrete for the manufacture of drain tile, sewer tile, septic tanks, etc., exposes it to the dissolving action of solutions of many different kinds of acids. Professor Orton in discussing this subject with reference to drain tile says that cement drain tile are exposed persistently to the very influence under which they deteriorate most rapidly, namely, the solvent power of water more or less saturated with carbon dioxide and organic acids which tend to leach out the lime.<sup>2</sup>

In answer to this E. S. Hanson says, "that in the first place drainage water in farming communities is very far from being saturated with carbon dioxide, which is by the way the weakest of all acids."<sup>1</sup> Typical analyses of drainage water from cultivated fields are given by the U. S. Department of Agriculture, "Bureau of Soils Bulletin No. 26, Investigations in Soil Management, pages 23 to 77." The average from twelve wheat fields shows only 53.5 parts of carbonic and only 32.7 parts of organic matter in 1,000,000 parts of drain water. Samples taken from black marsh soil gave only 340.6 parts of  $H_2CO_3$  in 1,000,000 of water. The average amount of  $H_2CO_3$  in ground water and open ditches is less than 3 parts in 1,000,000. Chemical activity of such exceedingly weak acids is trifling and is not liable to attack the tile because of possible neutralization of the acid by lime in the soil. The analysis shows three times as much lime as carbonic acid in solution and carbonic acid would react with lime already in solution before it would attack solid lime in a tile. These figures given by Mr. Hanson are rather misleading unless we notice the fact that 53.5 parts in 1,000,000 for example means 53.5 milligrams of carbonic acid in a liter.

C. B. Mc Vay in an address delivered at Des Moines, Iowa, arguing in favor of the use of concrete for drain tile, contends that the active





parts of cement are the silicates, aluminates, and ferrates of calcium and when these become hydrolyzed they are in the form of crystals and colloids.<sup>10</sup> We then have a matrix of crystals and colloids holding the sand particles and gravel together, the whole forming a mass of great hardness and strength. Since sand and gravel have been submitted to the action of the elements, it remains to show the indestructibility of the matrix.

The basic element of this matrix is calcium or lime and while lime as lime hydrate (common slaked lime) is quite soluble in water, it is practically insoluble in the form of the hydrated silicates, aluminates and ferrates that compose the matrix. Water that has been in the soil for some time has already become saturated with soluble mineral salts, and rain water (which has considerable power as a solvent and always contains  $\text{CO}_2$ ) let us see what effect this would have on our tile. The concrete being more or less porous readily admits the water through its interstices. It may be taken for granted that the cement contains lime; it may also be taken for granted that hydrated calcium silicates, aluminates and ferrates are slightly soluble. What is the result? The  $\text{CO}_2$  in the water precipitates the lime as carbonate; this fills the pores of the concrete arresting further action by water. It is this principle that renders concrete when exposed to the weather more and more nearly impermeable to moisture as the years pass. This will in time make the tile too dense to take water only at the joints. In this presentation Mc Vay ignores the fact that the conditions which precipitate the lime as carbonate continue to be present, resulting in the formation of bicarbonate of lime which is soluble, hence the tendency would be to make the concrete more porous as time goes on.

W. R. Baldwin carried out an experiment which tends to confirm this puddling effect of water on concrete as explained by Mr. Mc Vay.<sup>5</sup> He made a cylinder 13 inches in diameter, 6 inches in thickness of Portland cement and



crushed ballast 1 to 4 varying in fineness. It was fitted into a water-tight steel ring 13 1/2 inches internal diameter and 6 inches in height. The test piece was fitted on a heavy cast-iron ring and connected to a reservoir above. This reservoir was surmounted by a heavy cast-iron stem, the upper end of which was connected with a gland in which a plunger was arranged so known weights could be piled on top and the descent of the piston recorded. For a constant pressure he came to the following conclusion: For a constant pressure of moderate magnitude, the flow at any time varies inversely as the time from the commencement of the experiment, but with a sudden change in pressure there is a corresponding variation in the flow. Toward the end of the experiment small stalactitic growths appeared on the under side of the test-piece and the percolation was so slow that no water fell into the drip-pan, the water being evaporated from the under side as quickly as it percolated through. The experiment appears to show that, at or near the surface of the concrete, and under moderately high pressure the water dissolves out some of the material of concrete but under the reduced pressure which prevails in the pores at some distance from the surface the dissolved material is precipitated on the sides of the pores reducing the flow and eventually checking it. A similar experiment was carried out by the writer and it will be fully discussed under the experimental work.

Another interesting case of the deterioration of concrete by acids produced by the decomposition of organic matter was reported by W. S. Mc Harge, of Chicago.<sup>15</sup> While directing an excavation along one wall of a concrete septic tank which had been in service between four and five years, he found the wall to be in such a badly weakened condition that it collapsed from the pressure of the contents of the tank when the backfill against it had been removed. The concrete was well made with good cement and had shown no previous signs of deterioration. Mr. W. S. Shields, 1907, has recently discovered similar serious in-





jury to two other septic tanks built about five years ago.<sup>15</sup> These tanks receive only domestic sewage, containing no trade waste. Further investigation of the effect of sewage on concrete is contemplated and will be fully justified by the importance of its bearing on sewer construction generally.

The following table, furnished to "The Blackmer & Post Pipe Company", of St. Louis by S. V. Peppel, Chemical Engineer of Columbus, Ohio, is very suggestive and may be taken as an indication of what would happen to a concrete sewer tile in actual use.

Sample "A" represents a semi-dry pressed pipe.

Sample "B" represents a reinforced poured concrete pipe.

Sample "C" represents a vitrified clay sewer pipe.

Hygroscopic water, or mechanical moisture in the air, dry samples as received.

Percentage on dry weight.-

"A"	"B"	"C"
0.54%	0.99%	0.54%

Absorption of water in seventy-two hours.

"A"	"B"	"C"
13.29%	5.65%	4.48%

Loss by aqueous extraction during absorption test.

"A"	"B"	"C"
0.60%	0.00%	0.00%

Loss to a One Per Cent Acetic Acid solution on being soaked for different periods of time.

	"A"	"B"	"C"
12 hrs.	1.68%	0.40%	0.00%
24 "	1.79%	0.80%	0.00%



Loss to a One Per Cent Hydrochloric Acid solution (1.20 specific gravity sol.) on being soaked for different periods of time.

	"A"	"B"	"C"
12 hrs.	2.50%	1.25%	0.00%
24 "	2.50%	1.76%	0.00%

Loss to a Five Per Cent Acetic Acid solution on being soaked for different periods of time.

	"A"	"B"	"C"
6 hrs.	5.01%	1.81%	0.00%
12 "	7.74%	3.01%	0.00%

Loss to a Five Per Cent Hydrochloric Acid solution, (1.20 specific gravity sol.) on being soaked for different periods of time.

	"A"	"B"	"C"
6 hrs.	7.59%	6.78%	0.00%
12 hrs.	8.66%	7.04%	0.00%

Not only is Portland cement disintegrated by acids which occur in drainage solutions but the alkali waters, such as occur in some of our western states, have a marked influence on it. J. Y. Jewett gives a typical example from the cement and concrete work of the United States reclamation service.<sup>23</sup> The Sun River projects in Montana near the city of Great Falls where a number of small structures, such as culverts, which are partially submerged in the small streams carrying the drainage of the surrounding country, have become softened where constantly submerged for a period of three to four months and show a breaking up of the structure at the line where the water rises and falls, that is, where there is alternate submersion and drying out. The result is similar in appearance to the effect of freezing and thawing only much more severe. It is caused by the formation of minute crystals whose expansive force is enormous but which disintegrate to a fine powder on being exposed to the air. An analysis of the water in mg. per liter is as follows: 1690 Ca SO<sub>4</sub>, 6870 Mg SO<sub>4</sub>, 305 Mg H<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>, 192 Mg Cl<sub>2</sub>, 20 K Cl. Total solids 9077. Weight after ignition





8855. Loss on ignition, 222. The principal mineral ingredient,  $\text{CaSO}_4$ , leads to the conclusion that the effect of the water on the concrete is similar in its action to sea water with the production of a calcium sulph-aluminate whose crystallization gives rise to swelling and cracking of the material.

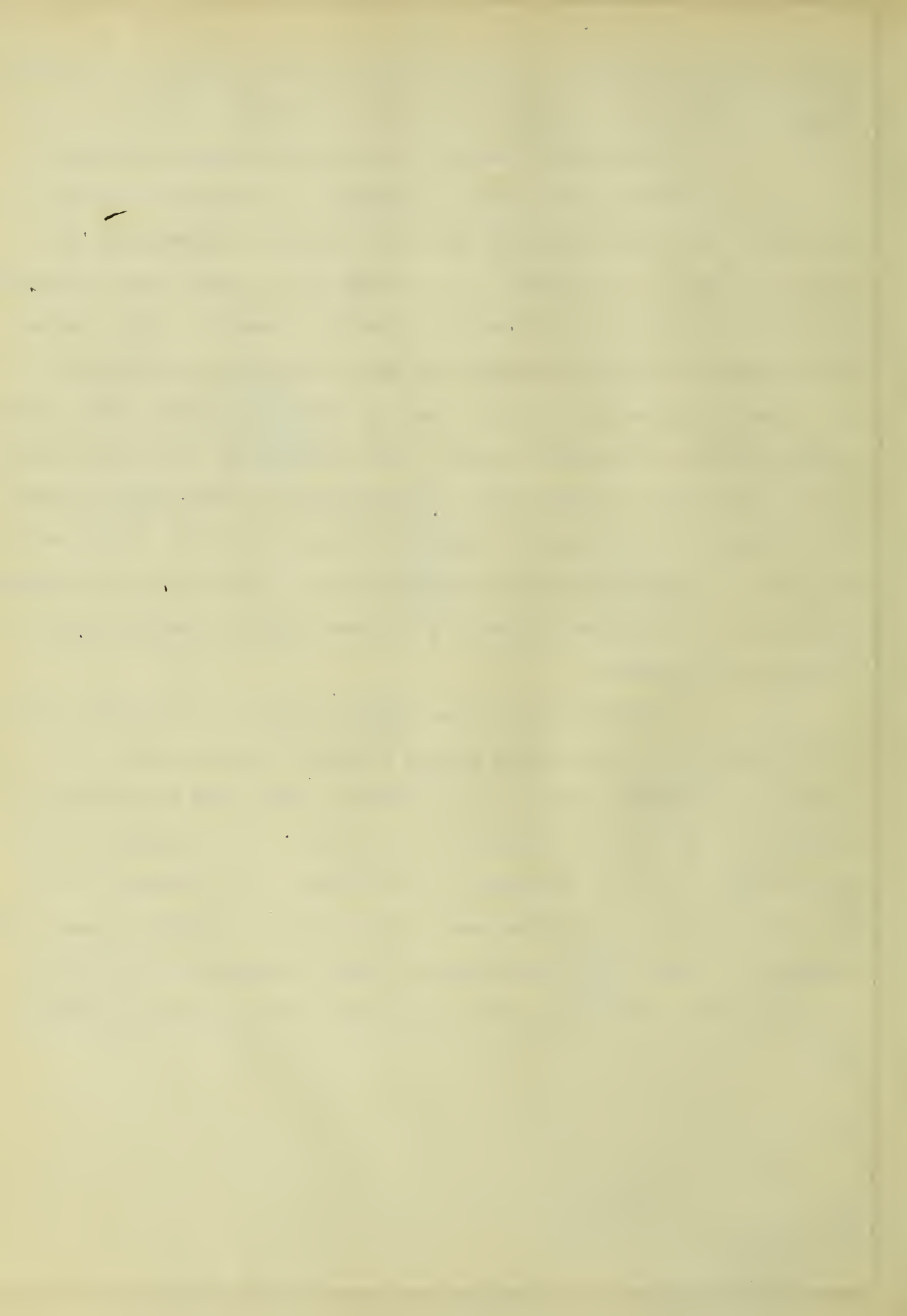
The question of the solubility of cement in pure water was brought forward by Messrs. G. G. and A. J. Wheat in a paper read before the Iowa Brick and Tile Association, Des Moines, Iowa, 1908.<sup>28</sup> They sent a properly cured cement tile six months old to Dr. Knight of Cornell College, Mt. Vernon, Iowa, to be tested by soaking in pure water, containing no solids at all, and then making analysis of the water. Also to be tested using water whose per cent of solid matter was known, and determining whether additions of solid matter were obtained from the cement tile. These results were obtained: Seventy-three grams of tile were soaked in distilled water for 72 hours. The water was then filtered and 200 c.c., or about 7 oz., was evaporated to dryness in a weighed platinum dish. A careful drying and weighing showed .0325 gr. had dissolved. At this rate the tile, were the entire 73 gr. pure cement, would dissolve in about 18 years. An analysis of this solid matter showed the following; Silica .004 gr.; iron and aluminum .0014; calcium .0085. No magnesium was found, but qualitative analysis showed the presence of sulphates, but these were not determined. Again the same piece, 73 gr., was left to soak for 95 hours in distilled water and 185 c.c. evaporated to dryness showed that .0390 gr. had dissolved. The rate of dissolving continued almost exactly the same. Two more similar determinations were made, using the city water as the solvent. The city water contained carbon dioxide and .0749 gr. of solid matter in 200 c.c. After 74 hours soaking in city water there was dissolved .0039 gr. After 96 hours in the city water .0320 gr. Each of these results show that the tile dissolved more slowly in the city water than in the distilled water. This experiment is interesting in that it gives quantitative data of experiments



with a concrete tile, both in distilled water and water containing the ordinary solids.

In this brief review of the literature enough has been given to show the conflicting opinions on the subject of the solubility of cement. But when we take into consideration the work of such able investigators as Le Chatelier and Dr. W. Michaelis, Jr., together with the many pieces of concrete work which have disintegrated under the influence of sea-water, there seems to be little reason to doubt that cement does deteriorate under its influence. Dr. Michaelis proposed to remedy this fault by substituting iron for the alumina, leaving the other constituents the same. On the other hand, it is quite certain, as other investigators contend, that if concrete work is porous enough to admit water readily and it is exposed to alternate freezing and thawing it will chip and crack just as rocks do under the same influence. It is probably true in climates where there is freezing and thawing in winter that both these causes operate to disintegrate concrete.

Although there are some cement advocates who claim that cement is not soluble to any great extent in weak solutions of mineral acids, most writers on the subject admit it is very soluble in these acids and also that it is soluble to some extent in weak acids like carbonic. The disputed question seems to be in regard to the extent of its solubility. The experiment carried out by Dr. Knight of Ames College seems to show that it is soluble in water containing the ordinary solids in solution and little carbonic acid.<sup>28</sup> The writer has made a study of this phase of the subject and it will be treated of farther on.





EXPERIMENTAL WORK.

Cement Analysis.

The cement selected for use in these experiments was the Atlas brand, a well known American Portland. For use in interpreting the results obtained in the various decompositions, a fairly complete analysis was made of the sample. It was first dissolved in HCl and then analysed as any silicate rock. The sample was dried for 1 hour at  $110^{\circ}$  in the air-bath.

Analysis of Atlas Cement, dried at  $110^{\circ}$ .

	A	B	Mean
SiO <sub>2</sub>	21.74%	21.66%	21.70%
Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	8.76%	8.90%	8.83%
CaO	62.16%	62.22%	62.19%
MgO	3.23%	3.30%	3.27%
SO <sub>3</sub>	1.72%	1.58%	1.65%
Loss on Ignition	<u>2.76%</u>	<u>2.82%</u>	<u>2.79%</u>
	100.37	100.48	100.43

In order to get definite results in a given time, it was necessary to make the laboratory conditions more extreme than any conditions to which concrete is usually subjected, but the attempt was made to keep them approximately the same, and thereby have the results indicative of what would happen when the test is less severe but lasting a very much longer time.

Puddling Effect of Carbonic Acid.

In order to test the effect of water percolating through a drain tile when this water has carbon dioxid dissolved in it, a tube of neat cement was made. The cement was mixed with just enough water to make it



mould well. It was then put into a large test-tube containing a smaller one which was not allowed to reach the bottom by about an inch. When the cement began to harden the inner tube was removed by a careful twisting motion and the outer tube was allowed to stand for two days. The glass was then carefully broken from the outside leaving a neat cement tube closed at one end, 15 centimeters long, 3 centimeters in diameter and having walls 7 millimeters thick. It was then put into water and allowed to remain four days and become thoroughly set. After allowing three weeks in which to become thoroughly cured, a rubber stopper bearing a glass tube was fitted into the open end. The stopper was wired in and then covered with Khatinsky cement to prevent leakage. The glass tube was now attached by means of rubber tubing to a bottle containing distilled water saturated with carbon dioxide under a pressure equivalent to 7 centimeters of mercury in addition to the atmospheric pressure. The manner of obtaining this pressure will be given in more detail in connection with another experiment. On account of the tube being neat cement the walls were very dense and the water passed through very slowly. It came at an average rate of one drop each thirty seconds. The flow continued about four or five days after which it gradually lessened with the formation of a white coating on the outside. Finally the flow stopped completely and the tube looked dry on the outside. A qualitative test of some scales of this material showed it to be nearly if not quite all  $\text{CaCO}_3$ .

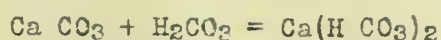
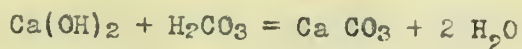
Two other similar tubes were made of 1:3 concrete. These were 8 inches long, 2 inches in diameter with walls a half inch thick. These tubes being made of concrete the walls were more porous than the first one. One of these was arranged exactly as the first one except that it was completely immersed in water in the drip jar. The walls, being more porous and surrounded with water, were not closed up in this case.





The third tube was arranged in a manner similar to the other two but attached this time to the faucet so that tap-water would percolate through instead of distilled water saturated with carbon dioxid. The pressure in this case was greater than before. This caused the water to run away in tiny streams. Inside of two hours white spots began to appear on the outside. These grew larger until at the end of eight days the tube was spotted with small white porous lumps of  $\text{CaCO}_3$ . It is possible that this carbonate may have come from the water as well as the concrete tube since the water has much  $\text{CaCO}_3$  dissolved in it. But the significant fact is that the pores in the tube were not closed up in this case as they were in the first case.

In the case of the first tube the solution of carbonic acid under pressure passing through the walls dissolved out the lime and become more or less saturated with it. The calcium silicate in contact with the water hydrolyzes and forms calcium hydroxid and silicic acid. The calcium hydroxide acts with carbonic acid forming the soluble acid carbonate thus:



When the solution reached the outer surface of the tube the pressure became diminished and the unstable acid carbonate decomposed into water,  $\text{CO}_2$  and  $\text{CaCO}_3$ , the latter being crystallized in the outer pores and on the surface and thus prevented any further flow. The experiment of passing carbonated water through a capillary tube drawn out to sufficient length and fineness so that one drop passed through every three or four seconds with the pressure the same as before was tried. Under these conditions the flow was not checked as before.

In the case of the second and third tubes, being made of concrete instead of neat cement, the pores were much larger. The water flowed through much more rapidly than in the first case. This, together with the fact that



they were immersed in water which tended to keep the carbonate from crystallizing out and filling the pores, was the reason why the flow was continuous. There seems to be little doubt that a concrete drain tile would act in the same way. It is usually made of 1:4 or 1:5 concrete and having a high porosity, the water would pass through rapidly. Drainage water has  $\text{CO}_2$  dissolved in it and since it soaks only through two or three feet of ground before coming to the tile it would have very little solid matter already dissolved in it. It is easily seen, therefore, that instead of the carbonate crystallizing in the pores of the tile and making it impervious to water, as Mc Vey suggests, the carbonate would be carried away at once by the water flowing inside the tile. This process would continue as time passed on rendering the concrete more porous until the bonding material would no longer be sufficient to hold the grains of sand together.

#### Solubility in Carbonic Acid.

The solubility of finely divided set cement was tested by taking a piece of neat cement which had been thoroughly set and allowed to stand for thirty days. This was ground up fine and dried in the air-bath at  $110^\circ$  for two hours. Three 5 gram samples were weighed out and put into 1 1/2 liter Florence flasks each containing about 1200 c.c. of distilled water. The flasks were fitted with rubber stoppers through which glass tubes passed and extended down near the bottom. The lower ends of the tubes were drawn down small to exclude the sample from the tube as much as possible. These glass tubes were connected by means of rubber hose and T tubes to a Kipp's generator. By fitting the upper opening of the generator with a rubber stopper and connecting it above to a jar used as a reservoir for acid, it was possible to get additional pressure on the  $\text{CO}_2$ . In this case as in the previous experiment a total pressure of seven centimeters of mercury in addition to the pressure of the





the atmosphere was used. The accompanying photograph shows quite clearly the form of the apparatus. The large bottle is the one to which the cement tube spoken of in the previous experiment was connected.

When the samples were first put into the flasks they were shaken until the water was nearly saturated with  $\text{CO}_2$  which had passed through one wash bottle. In order to give the water an opportunity to come freely into contact with both the cement and gas, the flasks were shaken vigorously three or four times daily. Care was taken in the beginning to give plenty of time for the water to become saturated, to find the greatest amount a liter would dissolve under these conditions. This was found to be 1.503 grams. On an average of about once every five days samples of 100c.c. were drawn out, filtered and evaporated in platinum dishes which had been previously dried in the oven at  $110^\circ$  for 1 hour; 1000c.c. were then siphoned out of each flask and the same amount of fresh distilled water returned each time and the flask connected with the generator again. The dried precipitates were weighed and the amount of dissolved substance determined by difference. This difference multiplied by eleven gave the total amount dissolved in the 1100 c.c. drawn out. This process was continued for approximately three months at the end of which time a liter only contained about .03 gr. The dissolved matter is very hygroscopic. As great care was required in weighing as is required in weighing a precipitate of aluminum oxide.



By evaporating down a quantity of the solution a sample of the





dissolved substance was obtained for analysis. It was dried and weighed out in the manner already described.

Analysis of Dissolved Substance.

	A	B	Mean
CaCO <sub>3</sub>	78.11%	78.43%	78.27%
SiO <sub>2</sub>	4.69%	4.46%	4.57%
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	3.65%	3.41%	3.53%
CaSO <sub>4</sub>	13.33%	13.21%	13.27%
MgO	<u>.52%</u>	<u>.61%</u>	<u>.56%</u>
	100.30%	100.12%	100.20%

To determine the actual per cent by weight of the sample that had dissolved, it was first necessary to deduct the weight of CaSO<sub>4</sub>. The remainder was then multiplied by .7827 to find the weight of Ca CO<sub>3</sub>. This was calculated to the oxide. The remainder is in the form in which it occurs in cement. The sum of these three parts, namely, Ca SO<sub>4</sub> + Ca O + (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>) gives the weight of the sample dissolved. The three samples used gave the following results:

Total dissolved Substance	4.5864 gr.	5.0037 gr.	4.6585 gr.
Ca SO <sub>4</sub>	.6182 "	.6640 "	.6219 "
Ca O	1.7709 "	1.9132 "	1.7811 "
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	.8779 "	1.0232 "	.8830 "
Actual amount of solid matter lost by the cement.	3.2670 "	3.6004 "	3.2859 "

When cement sets it takes up a great deal of water of hydration. This water forms a considerable portion of the total weight. In a series of



five tests run on Atlas cement the average amount of water of hydration was 9.55% of the original dry hydrated sample. Of the 5 gram, then, taken at the start, .4775 of a gram was water of hydration. This in the process of solution came out in the form of water and must be added in each case to the actual amount of solid matter lost by the cement.

	Sample I.	Sample II.	Sample III.
Actual amount of solid matter lost by the cement	3.2670 gr.	3.6004 gr.	3.2859 gr.
Water of Hydration	<u>.4775</u> "	<u>.4775</u> "	<u>.4775</u> "
	3.7445 "	4.0779 "	3.7634 "

The portion of the sample remaining in the flask in each case was filtered off, dried in the air-bath at 110° for 2 hours and weighed with the same kind of filter paper dried in the same way in the opposite pan. These results added to the total dissolved check pretty well with the original 5 grams taken.

	Sample I.	Sample II.	Sample III.	Mean
Total dissolved	3.7445 gr.	4.0778 gr.	3.7634 gr.	3.8617 gr.
Residue	<u>1.1721</u> "	<u>1.1598</u> "	<u>1.1790</u> "	<u>1.1706</u> "
	4.9174 "	5.2376 "	4.9424 "	5.0323 "

The results of this experiment show that set cement is acted upon by carbonic acid. Taking the average of the three results 77.23 per cent of the sample dissolved in the period indicated and there is every reason to believe that had the time been extended the dissolving action would have continued.

#### Solubility in Water.

The solubility of set cement in distilled water, without the ad-





dition of any  $\text{CO}_2$ , was next tried. A 5 gram sample was put into a flask as before and shaken occasionally. At the end of two weeks a determination similar to the others showed that .757 gr. per liter had dissolved. The 100c.c. removed were replaced by the same amount of fresh water and at the end of two weeks more another determination showed .615 grams per liter. This water, no doubt, contained some  $\text{CO}_2$  in solution so that it was decided to boil some distilled water vigorously for an hour to expell all  $\text{CO}_2$  and to try the same experiment. At the end of five days a determination showed .301 grams per liter dissolved. Three other determinations made at different intervals of time gave practically the same result. The results here show that the cement will dissolve in water containing no carbonic acid. The cement hydrolyses and the calcium silicate forms silicic acid and calcium hydroxide. The calcium hydroxide then dissolves.

#### Solubility in Solutions of Strong Acids.

It is claimed by some writers that cement is not soluble to any great extent by solutions of the mineral acids; they form an insoluble coating on the outside which completely protects the cement from further disintegration by the acids. In order to test this point pieces of 1:3 concrete varying in size from an inch cube to a three inch cube were put into a seven per cent solution of hydrochloric acid. The acid acted on the concrete rapidly at first, but the rate of action slowed down until it was hardly visible. But the acid solution gradually soaked through the pores until even in the larger piece at the end of ten days the bonding material was completely destroyed and the slightest pressure reduced it to a shapeless mass of sand. In case the concrete had any friction against it as in the case of a sewer tile the action would be much more rapid. In the case of neat cement pieces  $1\frac{1}{2} \times 1 \times 3$  inches long were used in the same



strength solution. An insoluble coating of silicic acid mixed with calcium shloride was formed. This coating being very soft rubbed off easily. It formed only a temporary protection for the cement as the acid gradually soaked into the interior and rendered the whole mass soft as putty.

#### Conclusions.

- I. Water saturated with carbon dioxide gas is a solvent for set Portland cement; the extent of solution seemingly depending upon physical conditions such as fineness of division of the material, length of time of contact, volume of water, etc.
- II. Mineral acid will penetrate throughout the mass of set concrete resulting in a disintegration of the same depending, of course, upon the reactive quantity of acid and cement.
- III. Pure water is a solvent for set Portland cement. The calcium silicate hydrolyses and forms silicic acid and calcium hydroxid. The former comes out in calloidal solution and the latter is directly soluble. The extent of the solubility depends upon the removal of the saturated water and its renewal by fresh water.



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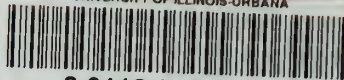








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